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(54) [Title of the Invention] Optical Recording Medium

(57) [Abstract]

[Means for Solution] An optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye, a light reflecting layer, and a protective layer are successively stacked, said optical recording medium characterized in that the light reflecting layer is comprised of a thin metal layer and a silver reflecting layer.

[Effects] A high reliability optical recording medium excellent in light resistance and high temperature and high humidity resistance can be produced at a low cost.

[CLAIMS]

[Claim 1] An optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye, a thin metal layer, a light reflecting layer, and a protective layer are successively stacked.

[Claim 2] An optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye, a thin metal layer, a light reflecting layer, a metal layer, and a protective layer are successively stacked.

[Claim 3] An optical recording medium as set forth in claim 1 or 2, wherein the thin metal layer is a metal layer comprised of Ti, V, Cr, Cu, Zn, or W of a thickness of 0.1 nm to 5 nm.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention] The present invention relates to a high reliability, inexpensive optical recording medium excellent in light resistance and high temperature and high humidity resistance.

[0002]

[Prior Art] Optical recording media such as compact disks have been widely used in the past as media for audio software, computer software, and electronic publishing due to their large storage capacity and high productivity as software packages. To produce conventional read only optical recording media such as compact disks, dies for transferring recordings to their transparent substrates are necessary. The cost per disk ends up becoming considerably high when producing about several hundred disks due to the costs of die fabrication.

[0003] In order to solve this problem, rather than produce recording disks through dies, optical recording media provided with recordable areas enabling direct recording on the disk, i.e., optical recording media able to be recorded by laser light known as "recordable compact disks" (hereinafter

referred to as "CD-Rs"), are being developed. Below, the explanation will be made with reference to the example of CD-Rs. CD-Rs can be recorded on and exhibit similar reflectivities as read only compact disks, so have the features that they can be recorded with information and can be played back and read by read only compact disk players and read only compact disk drives. Recordable optical recording media such as CD-Rs are usually produced by successively stacking on a transparent substrate a light absorbing layer including an organic dye, a light reflecting layer which consists of a metal, and a protective layer which consists of a UV curing resin.

[0004]

High Reflectivity ≥ 65% @ 780nm.

[Problems to be Solved by the Invention] In the already commercialized and marketed CD-Rs, to obtain a high reflectivity of at least 65% with respect to laser light of a wavelength of 780 nm for reading and to prevent a decline in reflectivity due to migration or chemical reaction of the light reflecting layer, gold, which has stability, or an alloy mainly comprised of gold is used as the light reflecting layer. Gold, however, is expensive, so becomes an obstacle when reducing manufacturing costs. On the other hand, when reducing manufacturing costs by using silver, aluminum, copper, or another metal having a reflectivity equivalent to gold or an alloy mainly comprised of the same for the light reflecting layer, a decline in reflectivity, increase in error, or other changes in the disk properties along with time easily occur due to migration or chemical reaction, so it was difficult to produce a high reliability CD-R able to withstand long term storage.

[0005] As opposed to this, to improve the corrosion resistance, it has been proposed to use a corrosion resistant alloy such as stainless steel, but most of these call for large amounts of additive ingredients for exhibiting the corrosion

resistance, so the reflectivity of the alloy becomes low. Moreover, since an anticorrosion mechanism forms a passive film on the surface of the alloy, when used as a reflective film, a decline in reflectivity was unavoidable. Further, when using gold, the reflectivity declines as the wavelength becomes shorter than the 780 nm wavelength of laser light currently being used for recording and reading. Therefore, in optical recording media of higher recording densities than the current CD-Rs, expected to be commercialized in the future, since it is expected that shorter wavelength recording and reading lasers will be used, use of gold for the reflecting layer will not necessarily be preferable. Use of a metal having a high reflectivity over the entire visible light area such as silver or aluminum for the reflecting layer will be preferable.

[0006]

[Means for Solving the Problem] The present invention was made in consideration of the above prior art and has as its object to inexpensive produce a recordable optical recording medium by using silver, which is less expensive than gold, as the light reflecting layer while maintaining a durability and reliability equivalent to an optical recording medium using high stability gold as the light reflecting layer and to provide an optical disk designed for high density recording by improving the light reflectivity in a broader wavelength range.

[0007] The present inventors engaged in intensive studies regarding the above problems and as a result discovered that by forming, in an optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye and a silver reflecting layer are stacked, a metal layer comprised of Ti, V, Cr, Cu, Zn, or W of 0.1 nm to 5 nm thickness at the interface of the light absorbing layer and silver reflecting layer, it is possible to produce a recordable optical recording medium giving a high reflectivity in a broad

wavelength range and experiencing little decline in reflectivity and thereby completed the present invention.

[0008] Namely, the present invention relates to (1) an optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye, a thin metal layer, a light reflecting layer, and a protective layer are successively stacked; (2) an optical recording medium comprised of a substrate on which a light absorbing layer which contains an organic dye, a thin metal layer, a light reflecting layer, a metal layer, and a protective layer are successively stacked, and (3) an optical recording medium as set forth in (1) or (2), wherein the thin metal layer is a metal layer comprised of Ti, V, Cr, Cu, Zn, or W of a thickness of 0.1 nm to 5 nm.

[0009]

[Embodiments of the Invention] Below, the optical recording medium according to the present invention will be explained in detail. The present invention is an optical recording medium comprised of a transparent substrate on which a light absorbing layer which contains an organic dye, a thin metal layer, and a silver reflecting layer are successively stacked.

[0010] As the material of the transparent substrate used for the present invention, in order to record and read a signal, a material with the high transparency of a refractive index to light of 1.4 to 1.6 or so, specifically, one with a value of light transmittance to visible light of 400 nm to 900 nm of 85% or more and little optical anisotropy is desirable. Specifically, a material with a high light transmittance to visible light such as a polyamide resin, a polycarbonate resin, a polymethyl methacrylate resin, a vinyl chloride resin, an amorphous polyolefin resin, or another plastic or glass can be suitably used. Among these, from the viewpoints of the strength of the substrate, ease of imparting guide grooves

or read only signals etc., and economy, an injection molded substrate made of an acrylic resin, polycarbonate resin,or polyolefin resin is desirable. In particular, a polycarbonate resin is desirable. These transparent substrates may be sheets or films, but normally ones of a thickness of 1 to 2 mm or so formed with concentric or spiral guide grooves or pits are used. These guide grooves or pits are preferably providded at the time of formation of the transparent substrates, but it is possible possible to provide them on the transparent substrates by coating a UV curing resin layer, stamping this by a stamper, then exposing the layer to UV light. When using the medium as an ordinary CD-R, the substrate is a disk shape of a thickness of about 1.2 mm and a diameter of about 80 to 130 mm provided at its center with a hole of a diameter of about 15 mm.

[0011] As the material of the light absorbing layer, organic dyes such as a phthalocyanine dye, naphthalocyanine dye, cyanine dye, polymethine dye, naphthoquinone dye, squarylium dye, croconium dye, azulenium dye, triarylamine dye, anthraquinone dye, metal-containing azo dye, dithiol metallic complex dye, India aniline metal complex dye, intermolecular CT dye, etc. are suitable. These are used alone or mixed in two or more types. The fact that these dye materials are usually used with an antidegradant, binder, etc. added is understood by a person skilled in the art. As the method of forming the light absorbing layer containing an organic dye, the method of dissolving the organic dye in an organic solvent and spin coating this on the transparent substrate directly or via another layer can be suitably used.

[0012] The fact that the thickness of the light absorbing layer is suitably selected according to the recording mode, the wavelength to be used, the optical constant of the reflecting layer, and the material of the light absorbing layer in

consideration of the record sensitivity and performance coefficient with respect to the power of the recording light such as the laser light used for recording will be easily understood by a person skilled in the art and normally is 10 nm to 5 Φm. The fact that adjustment is easily possible in spin coating by changing suitably the concentration of the solution of the organic dye dissolved in the organic solvent or the speed at the time of spin coating or, when using vapor deposition, changing suitably the vapor deposition time or the power at the time of vapor deposition will be understood by a person skilled in the art. Further, the light absorbing layer may be provided at one side of the transparent substrate or may be provided at both sides.

[0013] In the present invention, a light reflecting layer is formed on the light absorbing layer. The light reflecting layer may be formed directly or after formation of a light interference layer for the purpose of improving the recording characteristics. The light reflecting layer in the present invention consists of a metal layer and a silver reflecting layer. Hereafter, the explanation will be given of the light reflecting layer, that is, the silver reflecting layer, and metal layer in the present invention.

[0014] The methods of forming the silver reflecting layer and metal layer in the present invention include the wet method and dry method. The "wet method" is the general term for plating and is the method of causing precipitation of silver or metal from a solution to form a film. Giving a specific example, there is a silver mirror reaction. On the other hand, the "dry method" is the general term for vacuum film formation. Giving specific examples, it includes resistance heating vacuum deposition, electron beam heating vacuum deposition, ion plating, ion beam assist vacuum deposition, sputtering, etc.

[0015] In the present invention, when considering industrial processes such as washing off the plating solution at the time of manufacture, a vacuum film forming method is desirably used for formation of the silver reflecting layer and metal layer. Sputtering, which is excellent in metal adhesion, is the most desirable technique.

[0016] In vacuum deposition, the metal stock material is melted by an electron beam, resistance heating, induction heating, etc. and vapor pressure is raised to preferably not more than 0.1 mTorr (about 0.01 Pa) to cause vapor deposition on the substrate surface. In this case, it is also possible to introduce a gas such as argon at more than 0.1m Torr (about 0.01 Pa) and cause a high frequency or DC glow discharge.

[0017] In sputtering, DC magnetron sputtering, rf magnetron sputtering, ion beam sputtering, ECR sputtering, conventional rf sputtering, conventional DC sputtering, etc. can be used. In sputtering, for the stock material, it is sufficient to use a plate-shaped target of silver or metal. For the sputtering gas, helium, neon, argon, krypton, xenon, etc. can be used. Preferably, argon is used. The purity of the gas is preferably at least 99%, but 99.5% is more preferable.

[0018] The thickness of the silver reflecting layer is preferably 70 nm to 300 nm, more preferably 100 nm to 200 nm. If a too thin less than 70 nm, the thickness of the silver is not sufficient, so light will pass through and the reflectivity will decline. On the other hand, even if the thickness is made more than 300 nm or too thick, the reflectivity will not rise and saturation will be exhibited. This is not desirable in terms of the efficient utilization of resources and manufacturing costs.

[0019] The silver reflecting layer may include, to an extent not impairing its function, gold, copper, nickel, iron, cobalt, tungsten, molybdenum, tantalum, chromium, indium, manganese,

titanium, aluminum, or other metal impurities.

[0020] The thickness in the present invention is measured by a contact stylus roughness meter, repeat reflective interferometer, microbalance, quartz resonator method, etc. With the quartz resonator method, the thickness can be measured during film formation, so this is suitable for obtaining the desired thickness. Moreover, there is the method of setting the conditions of film formation beforehand, forming the film on the sample substrate, investigating the relationship between the film formation time and thickness, then controlling the film by the film formation time.

[0021] The present invention is characterized by introducing a metal layer of an amount effective for preventing a decline in the light reflectivity due to migration or a chemical reaction of the silver between the organic dye and silver reflecting layer. The "metal layer" in the present invention is an extremely thin metal layer of an amount effective for preventing a decline in the light reflectivity.

[0022] As the metal used for the metal layer, Mg, Al, Si, Be, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Cd, In, Sn, Sb, Te, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Hf, Ta, W, Re, Os, Ir, Pt, Au, Ti, Pb, Bi, Po, U, etc. may be mentioned. Among these Ti, V, Cr, Cu, Zn, and W are preferable. Note that these may be used alone or in combinations of a plurality of metals for a mixed metal layer.

[0023] The thickness of the metal layer is preferably not less than 0.1 nm and not more than 5 nm, more preferably not less than 0.1 nm and not more than 2 nm. If the metal layer is a too thin less than 0.1 nm, it is not possible to obtain a sufficient light reflectivity after the endurance tests. Further, if the metal layer is a too thin more than 5 nm, the initial light reflectivity (reflectivity at time of

production) falls and it is difficult to obtain the function as an optical recording medium of the present invention. Note that the sufficient light reflectivity spoken of here means a reflectivity of at least 90% of the reflectivity before the endurance tests when using only a silver reflecting layer, not using a metal layer, for the reflecting layer.

[0024] Here, since the thickness of the metal layer is extremely thin, it is difficult to directly find the actual thickness from a sample after film formation. Therefore, the film formation conditions were set in advance, a film was grown on the sample substrate to a thickness of an extent where the thickness could be directly measured, the relationship between the film formation time and the thickness was investigated, then the thickness at a shorter film formation time was estimated. Further, the thickness obtained by the quartz resonator method was used as it was. These may differ from the actual thickness, so can be called estimated thicknesses.

[0025] What is important here is the following two points. First, the metal film must not be formed so thick that a sufficient light reflection can no longer be obtained. Second, a metal effective with respect to a humidity and heat resistance test, a light irradiation test, or other endurance tests should be interposed between the light recording layer including the organic dye and the silver reflecting layer.

[0026] In reality, since the metal layer is extremely thin, it does not exist as a sufficiently continuous film (continuous layer) and rather may be considered to be discontinuous like an island-structure, but even so a sufficient effect is exhibited. Here, this will also be expressed as a "film (layer)".

[0027] Since the metal layer is extremely thin, it is extremely unstable. Therefore, even in continuous production in a vacuum, it is easily deduced that part or almost all undergoes oxidation

etc. Further, the metal layer is extremely thin compared with the silver reflecting layer, so a clear layer structure is not obtained and the metal layer may also exist as a mixed layer with part of the surface of the silver. The metal layer and silver reflecting layer are formed on the light absorbing layer directly or via another layer.

possible mixed surface

[0028] Further, another metal layer may be interposed between the light reflecting layer and the protective layer. This metal layer may basically be formed thin in accordance with the above-mentioned metal layer. Note that this metal layer may also be formed thicker than the above.

[0029] As the protective layer formed on the silver reflecting layer or metal layer, an acrylic UV curing resin or other hard material is preferably used. Normally, this is formed by coating the light reflecting layer directly or via another layer by spin coating to a thickness of 2 to 20 μm, then curing by UV irradiation.

[0030] Further, in accordance with need, coating the interface of the organic dye and metal layer, the interface of the protective layer and silver reflecting layer, and the interface of the protective layer and metal layer with a surface treatment agent for the purpose of prevention of a reaction with the existing silver or prevention of migration of silver so as to prevent a decline in the reflectivity of the silver does not inhibit the working of the present invention in any way.

[0031] The optical recording medium produced in the above way preferably has a reflectivity of light at 770 to 830 nm of at least 65% before and after the endurance tests. A current CD-R preferably has a reflectivity at 780 nm of at least 65% before and after the endurance tests. Further, an optical recording medium designed for higher density using a laser light of a wavelength shorter than the 780 nm laser light used for current CD-Rs preferably has a reflectivity which does

not change more than 10%, preferably not more than 5%, before and after the endurance tests.

[0032] The "endurance tests" in the present invention is for example a 500 hour humidity and temperature resistance test at a humidity of 85% and a temperature of 85EC and a 100 hour light resistance test of irradiation of simulated light of five times the energy of sunlight (5 suns).

[0033]

[Examples]

[Example 1] As the transparent substrate, a polycarbonate substrate with a diameter 120 mm and a thickness of 1.2 mm provided with a spiral tracking groove for a recordable compact disk was used. For the light absorbing layer, a phthalocyanine dye, i.e., a 3.5 wt% dimethyl cyclohexane solution of Pd-phthalocyanine having one 1-isopropyl-isoamyloxy group at each α-position of the four benzene rings which constitute phthalocyanine, was spin coated on a polycarbonate resin substrate (disk of diameter of 120 mm and thickness of 1.2 mm) provided with a guide groove at 2000 rpm, then dried at 70°C for 2 hours to form a light absorbing layer of 100 nm thickness.

[0034] This recording layer had formed on it a titanium metal layer of 3 nm by attaching a titanium target to a Balzars sputtering apparatus (CDI-900). Subsequently, the titanium metal layer had formed on it a silver reflecting layer to 100 nm by attaching a silver target to the Balzars sputtering apparatus (CDI-900). In this manner, a light reflecting layer which consists of a titanium metal layer and a silver reflecting layer was formed. This light reflecting layer was spin coated with a UV curing resin SD-17 (made by Dainippon Ink and Chemicals), then irradiated with ultraviolet light to form a protective layer of 6 μm and thereby produce the optical

recording medium.

[0035] The optical recording medium was recorded with an EFM signal by a linear velocity of 2.8 m/s and a laser power of 9.5 mW using a Philips writer (CDD-521) carrying a 780 nm semiconductor laser head. The obtained optical recording medium was subjected to a high temperature and high humidity test for 500 hours under conditions of a temperature of 85°C and a humidity of 85% and was subjected to a light irradiation test of 5 suns (500 mW/cm^2) at 60°C for 100 hours and measured for the change in the reflectivity and C1 error before and after the tests. As a result, just a slight decline in reflectivity and increase in C1 error were seen both after the high temperature and high humidity test and after the lightl irradiation test. The results are shown in Table 1.

[0036] [Example 2] Except for using tungsten of 3 nm for the metal layer, the same procedure was followed as in Example 1 to produce an optical recording medium. Furthermore, this optical recording medium was evaluated in the same way as Example 1, whereupon only a slight decline in the reflectivity and increase in the C1 error were seen. The results are shown in Table 1.

[0037] [Example 3] Except for using copper of 3 nm for the metal layer, the same procedure was followed as in Example 1 to produce an optical recording medium. Furthermore, this optical recording medium was evaluated in the same way as Example 1, whereupon only a slight decline in the reflectivity and increase in the C1 error were seen. The results are shown in Table 1.

[0038] [Comparative Example 1] Except for not forming a metal layer and making the light reflecting layer only a silver reflecting layer, the same procedure was followed as in Example 1 to produce an optical recording medium. Furthermore, this optical recording medium was evaluated in the same way as

Example 1, whereupon a remarkable decline in the reflectivity and a large increase in the Cl error were seen. The results are shown in Table 1.

[0039] [Comparative Example 2] Except for using titanium of a thickness of 20 nm for the metal layer, the same procedure was followed as in Example 1 to produce an optical recording medium. Furthermore, this optical recording medium was evaluated in the same way as Example 1, whereupon the reflectivity did not reach 65% and did not satisfy the specifications of present CD-Rs.

[0040]

[Table 1]

Table 1

	Reflectivity			C1 error		
	Initial value	After light irradia-tion test	After humidity /heat resist-ance test	Initial value	After light irradia-tion test	After humidity /heat resist-ance test
Ex. 1	71	69	68	3	10	12
Ex. 2	72	69	68	2	5	15
Ex. 3	73	68	69	2	6	18
Comp. Ex. 1	75	65	63	3	188	179
Comp. Ex. 2	58	-	-	-	-	-

[0041]

[Effect of the Invention] As clear from the examples and comparative examples, according to the present invention, a high reliability optical recording medium which is excellent in durability can be produced without using the gold which had been used for conventional light reflecting layers and

so the present invention is extremely useful in industry.